Physico-chemical properties and transition metal complex formation in alkali pyrosulfate and hydrogen sulfate melts

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The molten salts $\text{M}_2\text{S}_2\text{O}_7$ and MHSO$_4$, the binary molten salt systems $\text{M}_2\text{S}_2\text{O}_7$-MHSO$_4$ and the molten salt-gas systems $\text{M}_2\text{S}_2\text{O}_7$-V$_2$O$_5$ and $\text{M}_2\text{S}_2\text{O}_7$-M$_2$SO$_4$-V$_2$O$_5$ ($\text{M} = \text{Na, K, Rb, Cs}$) in O$_2$, SO$_2$ and Ar atmospheres have been investigated by thermal methods like calorimetry, Differential Enthalpic Analysis (DEA) and Differential Scanning Calorimetry (DSC). Fundamental thermodynamic data like temperatures and molar heats of solid-solid transition and fusion, phase diagrams, heat capacities of solids and liquids, heat of mixing, and heats of complex formation have been obtained and are reviewed here. Also EPR spectroscopic evidence of V(IV) complexes and their structure are reported and the results are discussed in relation to the mechanism of SO$_2$ oxidation by V$_2$O$_5$ based industrial catalysts.

Keywords: Alkali pyrosulfates, alkali hydrogen sulfates, vanadium pentoxide, EPR spectroscopy, complex formation

Introduction

The molten salt-gas system $\text{M}_2\text{S}_2\text{O}_7$-MHSO$_4$-$\text{M}_2\text{SO}_4$-$\text{V}_2\text{O}_5$ / SO$_2$-O$_2$-H$_2$O-N$_2$ ($\text{M} = \text{alkali}$) at 400–600ºC is considered a realistic model of the SO$_2$ oxidation catalyst under various conditions of industrial operation. Traditional industrial SO$_2$ oxidation catalysts have molar ratios in the range $\text{M}/\text{V} = 2$–4, where $\text{M}$ is usually a mixture of K and Na. In some cases also Cs is added in order to improve the activity at lower temperatures, i.e. below 420ºC, where precipitation of low soluble V(IV) and V(III) compounds has been shown to cause catalyst deactivation. The molten salt mixture $\text{M}_2\text{S}_2\text{O}_7$-MHSO$_4$ is also an excellent solvent for the dissolution of transition metal oxides. In the light of this we are currently investigating fundamental physico-chemical, redox and complex chemical properties as well as the catalytic activity of the general catalyst model system or part systems. We utilize spectroscopic, electrochemical and magnetic methods as well as thermal methods. Results of the latter method are reviewed here, focusing on the alkali metals Na, K, Rb and Cs, since Li is known not to form a stable pyrosulfate.

Experimental

Chemicals

Pure $\text{M}_2\text{S}_2\text{O}_7$ salts are either not commercially available (Rb, Cs) or seriously contaminated by hydrogen sulfates (Na, K) due to their hygroscopicity. Therefore, pure and dry $\text{M}_2\text{S}_2\text{O}_7$ was synthesized by thermal decomposition in dry N$_2$ atmosphere of commercial $\text{M}_2\text{S}_2\text{O}_8$ (Merck, p.a.), in the case of Na and K, while the non-commercially available peroxy-disulfates Rb$_2$S$_2$O$_8$ and Cs$_2$S$_2$O$_8$ were synthesized in the laboratory as earlier described. The commercial available NaHSO$_4$ and KHSO$_4$ (Merck, suprapur (99%)) were dried at 110ºC while the non-commercial available RbHSO$_4$ and CsHSO$_4$ were synthesized by adding carefully weighed amounts of water to the respective pyrosulfates in ampules. The ampules were then sealed and equilibrated by slow step-wise heating to 230–250 ºC. The purity was checked by Raman spectroscopy on the molten salt showing less than 0.5% residual pyrosulfate. All handlings of the hygroscopic alkali pyrosulfates and hydrogen sulfates were performed in a glovebox with a water content of less than around 5 ppm. All chemicals were kept on ampules, only opened in the glovebox, and resealed immediately after use.

Non-hygroscopic V$_2$O$_5$ (Cerac, pure (99.9%)) and alkali sulfates $\text{M}_2\text{SO}_4$ (Merck, p.a.) could be kept outside the glovebox and used without further treatment. Commercial gases of O$_2$, N$_2$, Ar, SO$_2$, and air were used and, when necessary, dried through P$_2$O$_5$ containing glass columns.

Thermal measurements

The temperatures of the phase transitions, solid-solid or solid-liquid, and the heat involved in these transitions have been measured by DEA (Differential Enthalpic Analysis) with a Calvet micro calorimeter. This apparatus has been described previously. The heat, $Q$, involved during the
phase transition is linked to the area, $S$, of the thermogram by the linear relation: $Q = KS$, where $K$ is the calorimeter constant. This constant is determined in a separate experiment with the same heating rate on a sample of lead. Temperature and enthalpy of melting of lead are $T_{fus} = 600 \text{ K}$ and $H_{fus} = 4.81 \text{ kJ mol}^{-1}$. The heat of mixing of the investigated systems was measured in the Calvet micrometer. Two methods were used: the direct drop and the indirect drop method. The device used for the indirect method is shown in Figure 1. By this method the added crystals of V$_2$O$_5$ were thermally equilibrated just above and at the same temperature as the melt. Then, by applying current to coil (1), the crystal dropped into the melt and the exchanged heat recorded and integrated graphically or by a connected data acquisition computer. Alternatively, the experiments were carried out by the direct drop method essentially performed by a set-up as shown in Figure 1, but omitting the intermediate tube. The calorimeter was calibrated at the end of each experimental series by direct drop of pre-weighted gold bullets to the melt. The partial enthalpy of liquid-liquid mixing $\Delta H_{\text{part}}(A)$, when a solid (A) is dropped from room temperature, $T_{\text{amb}}$, into a liquid at temperature $T$ and at constant pressure, is given by Equation [1]:

$$\Delta H_{\text{part}}(A) = \frac{\Delta H_{\text{part}}}{T}.$$  

where $\Delta H_{\text{exp}}$ is the experimentally measured heat, $n^A$ is the number of moles of component A added by each experiment, $C_p(A)$ is the heat capacity of A and $\Delta H_0(A, T)$ is the molar enthalpy of fusion of A extrapolated to the experimental temperature $T$. The molar heat of fusion of V$_2$O$_5$ (m.p. 670ºC), was found to be 61.65 kJ/mol and 62.16 kJ/mol, respectively at 430ºC and 470ºC, by extrapolation of the data in reference 9. Heat capacity measurements were carried out with a Setaram DSC 121 differential scanning calorimeter. The apparatus and the measuring procedure have been previously described in detail. The measuring method used was the so-called ‘step-method’, developed by Setaram. Quartz cells of 7 mm in diameter and 15 mm in length were filled in the glovebox, sealed under vacuum and then placed in the calorimeter. Measurements were performed by heating steps of 5 K followed by 400 s isothermal delay. The heating rate was 2 K min$^{-1}$. All experiments were started at 300 K and performed up to 750–800 K.

**EPR Spectroscopy**

Mixtures of M$_2$S$_2$O$_7$ and M$_2$SO$_4$ were prepared by melting and mixing the components in a sealed ampoule. V$_2$O$_5$ was added to this mixture at a M/V (M$_2$S$_2$O$_7$/V$_2$O$_5$) molar ratio of 40. The chemicals were filled into a quartz ampule (diameter = 12 mm, 300 mm length) in the glovebox and sealed immediately under $\text{ca.} 0.7$ bar SO$_2$. The sealed ampules were equilibrated for at least 100 hours just above the melting point of the mixture, i.e. 400–460ºC dependent on the type of alkali metal. From the furnace the ampules were dropped directly into icy water. After quenching, the ampules were cut open in the glovebox and some of the mixture ground and transferred to quartz capillary tubes (2.0 mm outer diameter, 0.5 mm wall thickness). The samples were sealed under vacuum. Samples with other M/V ratios were made by dilution of the M/V = 40 mixture with a premixed M$_2$S$_2$O$_7$-M$_2$SO$_4$ mixture.

Table I. Thermal properties of M$_2$S$_2$O$_7$ (M = Na, K, Rb, Cs). Temperatures, enthalpies and entropies of fusion, coefficients for the linear equations $C_p(s) = A + BT$ for the heat capacities of the solid state, heat capacities of the liquid state, associate temperature ranges and molar volumes

<table>
<thead>
<tr>
<th>M$_2$S$_2$O$_7$</th>
<th>$T_{fus}$ (K)</th>
<th>$\Delta H_{fus}$ (J mol$^{-1}$)</th>
<th>$\Delta S_{fus}$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$C_p(s)$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$C_p(l)$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$T$ range (K)</th>
<th>$V_{mol}$ ($T_{fus}$) (cm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S$_2$O$_7$</td>
<td>675</td>
<td>41700</td>
<td>62</td>
<td>110.2(36)</td>
<td>0.18(8)</td>
<td>300–590</td>
<td>244.8(10)</td>
</tr>
<tr>
<td>K$_2$S$_2$O$_7$</td>
<td>692</td>
<td>21200</td>
<td>34</td>
<td>134.7(10)</td>
<td>0.17(7)</td>
<td>300–590</td>
<td>267(2)</td>
</tr>
<tr>
<td>Rb$_2$S$_2$O$_7$</td>
<td>723</td>
<td>17800</td>
<td>25</td>
<td>207.4(12)</td>
<td>0.05(7)</td>
<td>300–700</td>
<td>272.2(18)</td>
</tr>
<tr>
<td>Cs$_2$S$_2$O$_7$</td>
<td>734</td>
<td>19500</td>
<td>27</td>
<td>147.5(19)</td>
<td>0.21(10)</td>
<td>300–710</td>
<td>292.3(43)</td>
</tr>
</tbody>
</table>

$^a$ Calculated as $\Delta H_{fus}/T_{fus}$.
Samples without SO$_4^{2-}$-saturation are sensitive to the decomposition of the solvent melt, due to the high vapour pressure of SO$_3$, which causes SO$_4^{2-}$-contamination of the M$_2$S$_2$O$_7$—especially at higher temperatures. The mixing procedure was the same as in the previous case, except that the samples were not remelted and requenched after being transferred to the capillaries as in the case of the M$_2$S$_2$O$_7$-M$_2$SO$_4$-(sat)V$_2$O$_5$/SO$_2$(g) system. No spectra of molten samples were recorded. It was not possible to record well resolved spectra with M/V ratios smaller than 160, the spectra smeared out due to increased spin-spin relaxation. The EPR spectra were recorded on a Bruker EMX spectrometer with a 12 kW 10$^9$/H$^1$1541/H$^1$1541 magnet. Room temperature Xband spectra were recorded with a Bruker ER4102ST cavity. High temperature X-band spectra were recorded with a Bruker ER4114HT cavity whereas the room temperature Q-band spectra were obtained with a Bruker ER5106Q cavity.

Results and discussion

M$_2$S$_2$O$_7$ (M = Na, K, Rb, Cs)

The data obtained on the alkali pyrosulfates are given in Table I. The coefficient for the heat capacity of solid K$_2$S$_2$O$_7$ was erroneously given in degrees Celsius in our previous publication on this subject. From the thermograms (DEA) obtained on K$_2$S$_2$O$_7$ and KHSO$_4$ the solid-solid $\beta \rightarrow \alpha$ transition is found for K$_2$S$_2$O$_7$ at 591 K and the temperature of fusion at 690 K, which, however, based on several measurements of the electrical conductivity (at the phase transition) is considered actually to be 692 K as given in Table I. Most of the information on the alkali pyrosulfates could not be found in the literature before or deviate largely from the values given here, e.g. the melting temperature of Cs$_2$S$_2$O$_7$ is 734 K compared to 553 K, the only value published previously.

The discrepancies are most probably due to serious contamination by hydrogen sulfates due to the hygroscopic properties of the alkali pyrosulfates. For K$_2$S$_2$O$_7$ the entropy of the $\beta \rightarrow \alpha$ solid-solid transition at 591 K is found to be 37 J mol$^{-1}$ K$^{-1}$, i.e. of the same size as the entropy of fusion of 31 J mol$^{-1}$ K$^{-1}$ found for at K$_2$S$_2$O$_7$. The sum of 68 J mol$^{-1}$ K$^{-1}$ is comparable to the entropy of fusion for Na$_2$S$_2$O$_7$ where no low temperature solid-solid transition is found. Therefore, the structure of $\beta$-K$_2$S$_2$O$_7$ and Na$_2$S$_2$O$_7$ are probably very similar while the structures of Rb$_2$S$_2$O$_7$ and Cs$_2$S$_2$O$_7$ probably are similar to the structure of $\alpha$-K$_2$S$_2$O$_7$ judged from their comparable melting entropies. However, only the X-ray structure of K$_2$S$_2$O$_7$ is reported in the literature, but very recently we have revealed from room temperature powder XRD on Na$_2$S$_2$O$_7$ that the two salts indeed have a very similar structure.

In addition to the thermal investigations, results from parallel density measurements are given in Table I in the form of the molar volume of the liquids at the melting temperature. A steady increase of the molar volume by increasing size of the cation is expected and indeed observed.

MHSO$_4$ (M = Na, K, Rb, Cs)

As for the alkali pyrosulfates DEA has been performed on the acid sulfates KHSO$_4$. As for K$_2$S$_2$O$_7$ the entropy of fusion for Na$_2$S$_2$O$_7$ and Na$_2$S$_2$O$_7$ are probably very similar while the structures of Rb$_2$S$_2$O$_7$ and Cs$_2$S$_2$O$_7$ probably are similar to the structure of $\beta$-K$_2$S$_2$O$_7$ judged from their comparable melting entropies. However, only the X-ray structure of K$_2$S$_2$O$_7$ is reported in the literature, but very recently we have revealed from room temperature powder XRD on Na$_2$S$_2$O$_7$ that the two salts indeed have a very similar structure.

Table II. Thermal properties of MHSO$_4$ (M = Na, K, Rb, Cs). Temperatures, enthalpies and entropies of fusion, coefficients for the linear equations $C_p(s) = A + BT$ for the heat capacities of the solid state, heat capacities of the liquid state and associate temperature ranges

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{\text{fm}}$ (K)</th>
<th>$\Delta_{\text{fm}H}$ (J mol$^{-1}$)</th>
<th>$\Delta_{\text{fm}S}$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$C_p(s)$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$T_{\text{range}}$ (K)</th>
<th>$C_p(l)$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$T_{\text{range}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHSO$_4$</td>
<td>455</td>
<td>17300</td>
<td>38</td>
<td>124.7</td>
<td>298–455</td>
<td>246</td>
<td>455–500</td>
</tr>
<tr>
<td>KHSO$_4$</td>
<td>a 488</td>
<td>16600</td>
<td>34</td>
<td>124.7</td>
<td>298–488</td>
<td>246</td>
<td>455–500</td>
</tr>
<tr>
<td>RbHSO$_4$</td>
<td>b 479</td>
<td>12770</td>
<td>27</td>
<td>124.7</td>
<td>298–488</td>
<td>246</td>
<td>455–500</td>
</tr>
<tr>
<td>CsHSO$_4$</td>
<td>c 491</td>
<td>9580</td>
<td>20</td>
<td>124.7</td>
<td>298–488</td>
<td>246</td>
<td>455–500</td>
</tr>
</tbody>
</table>

$^a$ $\Delta_{\text{fm}H}$ (451 K) = 2110 J mol$^{-1}$

$^b$ $\Delta_{\text{fm}H}$ (472 K) = 3855 J mol$^{-1}$

$^c$ $\Delta_{\text{fm}H}$ (451 K) = 6790 J mol$^{-1}$
other measured thermal parameters for the alkali hydrogen sulfates are shown in Table II. Again, only very little information, e.g. temperatures of fusion of NaHSO₄ and KHSO₄ have earlier been given in the literature or a large deviation is found compared to our values.

M₂S₂O₇-MHSO₄ (M = Na, K, Rb, Cs)

The phase diagrams of these binary systems are currently being investigated by us, using thermal, electrochemical and spectroscopic methods. The results for the K₂S₂O₇-KHSO₄ system is shown in Figure 3 as an example. The phase diagram shows considerable variations above x = 0.45 from the diagram of Hagisawa and Takai, which was obtained from differential enthalpic analysis only.

The diagram of Cambi and Bozza also deviates dramatically from ours, i.e., up to 55 K lower liquidus temperatures were found by these authors, probably because their DTA measurements were performed by cooling, leading to large subcooling before crystallization. Thermodynamic calculations show that the heat of the α → β transition at 591 K for K₂S₂O₇ is so large that the liquidus curve in the vicinity of the temperature, corresponding to x = 0.45 in the phase diagram, will exhibit a marked change in the slope. The eutectic composition could not be found accurately by the conductivity or thermal methods, but was alternatively found by spectrophotometry since O-H vibrations absorb rather strongly in the near infrared region. From spectra of the eutectic melt and a series of standards, prepared around the eutectic, the composition was found with high precision. All of the diagrams exhibit simple eutectic systems with a composition of the eutectics rather close to the pure alkali hydrogensulfate, i.e. x = 0.98, 0.94, 0.87 and 0.84 for M = Na, K, Rb and Cs respectively. The measurements and calculations point for both systems to an ordered liquid, most probably due to oscillating H-bonding between the species HSO₄⁻ and S₂O₇²⁻, dominating the liquid as illustrated by the equation:

<table>
<thead>
<tr>
<th>Liquid-liquid reactions</th>
<th>K (kJ mol⁻¹)</th>
<th>Cs (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₂O₅ + 2S₂O₇²⁻ → (VO)₂O(SO₄)⁴⁻</td>
<td>-89.2±1</td>
<td>-89.1±1</td>
</tr>
<tr>
<td>V₂O₅ + S₂O₇²⁻ + 2SO₄²⁻ → 2VO₂(SO₄)²⁻⁻⁻</td>
<td>-124±12</td>
<td>-166±12</td>
</tr>
<tr>
<td>V₂O₅ + 2S₂O₇²⁻ + SO₂ → 2VO(SO₄)²⁻ + SO₃</td>
<td>-180±20</td>
<td>-176±7</td>
</tr>
<tr>
<td>V₂O₅ + S₂O₇²⁻ + 3SO₄²⁻ + SO₂ → 2VO(SO₄)³⁻⁻⁻</td>
<td>-208±20</td>
<td>-228±7</td>
</tr>
</tbody>
</table>

Table III. Possible reactions and reaction enthalpies of the molten systems M₂S₂O₇-V₂O₅ and M₂S₂O₇-M₂SO₄(sat)-V₂O₅ (M = K and Cs) in Ar or SO₂ gas atmospheres*
All of the $\text{M}_2\text{S}_2\text{O}_7$-$\text{MHSO}_4$ systems exhibit melting temperatures of the eutectics some 250 K lower than the temperature of fusion of the alkali pyrosulfates, $\text{M}_2\text{S}_2\text{O}_7$ (M=Na, K, Rb, Cs), which may prove interesting for the design of low melting solvents for transition metal oxides.

$\text{M}_2\text{S}_2\text{O}_7$-$\text{V}_2\text{O}_5$ (M = Na, K, Rb, Cs)

The phase diagrams of these binary systems have been obtained by us for M = K, Rb and Cs \cite{1,2,3,4}, while the system based on Na is thermally unstable, decomposing to sulfates and gaseous SO$_3$ by increasing temperature and content of V$_2$O$_5$. Thus the pure Na-system could not be studied. The other systems have been studied by electrical conductivity measurements in various combinations with thermal and spectroscopic techniques. An example is shown in Figure 3 for M = K \cite{4,5}.

The phase diagram of the K$_2$S$_2$O$_7$-$\text{V}_2\text{O}_5$ system exhibits three maxima corresponding to the formation of compounds with the stoichiometry 3K$_2$S$_2$O$_7$•V$_2$O$_5$, 2K$_2$S$_2$O$_7$•V$_2$O$_5$, and K$_2$S$_2$O$_7$•V$_2$O$_5$. These compounds can most probably be attributed to, respectively, the formulas K$_3$VO$_2$SO$_4$S$_2$O$_7$, K$_4$($\text{VO})_2O(SO_4)_4$, and KVO$_2$SO$_4$ judged from previous \cite{20} single crystal X-ray investigations on the Cs-salt Cs$_5$(VO)$_2O(SO_4)_4$ and ongoing X-ray investigations\cite{21} on the analogous K and Rb salts and the compound Cs$_2$SO$_4$V$_2$O$_5$.

The phase diagrams of the Rb$_2$S$_2$O$_7$-$\text{V}_2\text{O}_5$ system and the Cs$_2$S$_2$O$_7$-$\text{V}_2\text{O}_5$ system, both exhibit only one maximum at = 0.33 corresponding to the formation of the compound M$_4$(VO)$_2O(SO_4)_4$ while the compound MVO$_2$SO$_4$ most probably might be formed in both systems at = 0.5. The structure\cite{20} of the vanadium oxo sulfato complex ion (VO)$_2$O(SO$_4$)$_4$\textsuperscript{4−} is shown in Figure 4. This complex seems to predominate\cite{22,23} in a very large composition range of all of the binary systems, including the range = 0.20–0.33 used for industrial SO$_2$ oxidation catalysts.

Heat of mixing in the systems M$_2$S$_2$O$_7$-$\text{V}_2\text{O}_5$ and M$_2$S$_2$O$_7$-$\text{M}_2\text{SO}_4$-$\text{V}_2\text{O}_5$ (M = K or Cs) in O$_2$, SO$_2$ or Ar

The heat of reactions forming the catalytic active vanadium oxo sulfato complexes and the heat of reactions involved in redox processes and sulfato complex reactions of these species have been measured by calorimetry. Both the indirect and the direct drop method were used to measure the liquid-liquid heat of mixing in the various systems. For the M$_2$S$_2$O$_7$-$\text{V}_2\text{O}_5$ systems (M = K and Cs) the heat of mixing has been obtained at several temperatures in the range 400–470ºC \cite{6,7,8} and in the composition region V$_2$O$_5$ = 0–0.5 in Ar, O$_2$ or SO$_2$ atmospheres. The reaction between the two components is very exothermic as illustrated by the measured values of the limiting partial molar enthalpies, i.e. the reaction enthalpies for the formation of the dimeric complex (VO)$_2$O(SO$_4$)$_4$\textsuperscript{4−}, as given in Table III. The formulas for the complexes given in Table III are all based on previous electrochemical, spectroscopic and structural
V(IV) in pyrosulfate melts were investigated by EPR spectroscopy. Based on the discussion above and an investigation on the composition and structure of the V(IV) complexes in the sulfate saturated system, but the line width is much smaller, whereas the line width in the sulfate saturated system. The spectra represent axial symmetric complexes as in the molten state at 450–460ºC. The Q-band spectra of the molten samples with M/V = 160 have been simulated using the SImpow computer program.

The general EPR features of the quenched samples are quite similar with two general trends. The X- and Q-band spectra both show axial symmetry typical for octahedral VO2⁺ complexes with the hyperfine structure (due to coupling to the ⁵¹V nucleus, I = 7/2), best resolved in the Q-band spectra. The line width of the spectra increases with increasing vanadium concentration (lower M/V ratio) and with the molar weight of the alkali cation. The samples Rb/V = 40, Rb/V = 80, Cs/V = 40 and Cs/V = 80 could not be recorded with well-resolved hyperfine structure in the X-band and are therefore not shown in Figure 5. The quenched spectra are typical immobilized axial symmetric spectra also known from, e.g. frozen vanadyl containing Schiff bases. Axial symmetric spectra can be well characterized by tensors and hyperfine coupling constants, i.e. the parameters g⊥, g∥, a∥, a⊥, and one line width.

The X-band spectra, stipulated in Figure 5, are computer simulations using these five parameters and assuming Lorentzian line shapes. No differences were found in the parameters dependent on the vanadium concentration (within experimental error), hence the best resolved spectrum for each alkali metal was used for the accurate calculation of the EPR parameters, regardless of the concentration. The quenched samples are identical within the experimental error of ±0.005 and ±10 for g and a respectively, i.e. g∥ = 1.930, g⊥ = 1.980, a∥ = 200 Gauss, a⊥ = 70 Gauss. Only the parameters of the parallel feature for the Cs-based samples deviate slightly.

It should be stressed, that observable in-plane anisotropy rarely occurs in EPR spectra, even though some rhombicity is present. However, the line width changes significantly by increasing size of the cation. The high temperature X-band EPR spectra (Figure 5) of the molten samples with M/V = 160 exhibit eight isotropic lines of varying intensity as always found for monomeric vanadyl complexes in solution. The different alkali pyrosulfate solvents seem not to affect the first coordination sphere of the complex.

Thus no variation in the isotropic g value or the isotropic hyperfine structure constant is observed as with respect to the type of the alkali cation. In some of the spectra, a skew baseline can be seen, probably due to part formation of dimeric or polymeric V(IV) species where coupling along the chains may smear out the hyperfine structure. The measured isotropic parameters fit well with the calculated isotropic values from the quenched samples considering the large temperature difference, indicating that we are dealing with the same complex in both phases.

The X- and Q-band EPR spectra of the vanadyl complexes without sulfate saturation are shown in Figure 6. The spectra represent axial symmetric complexes as in the sulfate saturated system, but the line width is much smaller, 6-15 G versus 20-50 G for samples with sulfate saturation.

This indicates that there is less distortion of the VO2⁺ unit for VO(SO₄)₂⁺ compared to VO(SO₄)₃⁻ complexes present in the sulfate saturated system. Furthermore, the EPR parameters of the parallel features are—not surprisingly—changed. The value of g⊥ is calculated to be typically
about 0.007 smaller in the case of VO(SO₄)₂²⁻ compared to VO(SO₄)₃⁴⁻. The perpendicular components are less affected. This shows that the character of the V=O bond is important for the relaxation path of the unpaired electron. This system seems to show the same trend on line width affected. This shows that the character of the V=O bond is affected. This system seems to show the same trend on line width affected. This shows that the character of the V=O bond is important for the relaxation path of the unpaired electron. This system seems to show the same trend on line width affected. This shows that the character of the V=O bond is important for the relaxation path of the unpaired electron.

Relation to catalysis and vanadium containing boiler deposits

During the catalytic oxidation of SO₂ to SO₃ the sulfate activity in the catalyst melt is of course lowered due to the reaction SO₃ + SO₂ → S₂O₇²⁻ being shifted to the right. At last bed conditions in sulfuric acid production the temperature is in the range 420–450°C which further stabilizes the S₂O₇²⁻ ion. Therefore, the M₂S₂O₇-V₂O₅ system and the redox reaction

\[ (VO)₂(SO₄)⁴⁻ + SO₃ → 2VO(SO₄)₂²⁻ + SO₄ \]

where SO₃ probably is solvated by S₂O₇²⁻ forming S₃O₁₀²⁻, seem particularly important. This reaction (Equation 6) has been studied spectroscopically for the K-system in the temperature range 435–480°C and a reaction enthalpy of –107 ± 4kJ/mol was obtained in good agreement with the calorimetric value of –91 ± 20 kJ/mol found here.

However, in the recently published reaction mechanism for SO₂ oxidation by alkali promoted vanadium based catalysts it is proposed that the reaction (Equation 6) is responsible for the deactivation of the catalyst while the catalytic cycle leading to the product probably only involves highly reactive V(V) complexes in rather low concentrations. Therefore, heat of reactions involving those individual V(V) complexes in the cycle cannot easily be obtained. The overall heat of reaction going through the catalytic cycle is of course not different from the heat of the oxidation SO₂ + 1/2 O₂ → SO₃, i.e. ΔH° = –98 kJ/mol.

The mechanism suggested in reference 3 has to be extended, thus a branch with the formation of the V(V) complex VO(SO₄)₃⁴⁻ at high SO₃ partial pressures should be included based on previous isolation of this compound from the K₂S₂O₇ - V₂O₅ system. This step may explain the inhibiting effect of SO₃ on the reaction rate observed experimentally as a negative kinetic reaction order for SO₃. The mechanism of catalytic SO₂ oxidation and the chemistry of fireside deposits of boilers fired with vanadium containing fuels like heavy fuel oil and Orimulsion has been exemplified by vanadium where oxo sulfato V(V) and V(IV) complexes have been identified and redox equilibria involving these complexes have been formulated. The possible role of these complexes for the reaction mechanism of catalytic SO₂ oxidation and the chemistry of deposits in power plant boilers has also been discussed.

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References

11. SETARAM DSC 121 - Experimentations, B03NEDSCF.